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<b>(54) Title:</b> METHOD OF PRODUCING PLASTICISED POLYVINYL ALCOHOL, AND ITS USE  <b>(57) Abstract</b>  The method of producing plasticised polyvinyl alcohol by mixing polyvinyl alcohol in the presence of an organic plasticiser and water in a quantity which is insufficient to dissolve the polyvinyl alcohol under normal conditions, includes the steps of: i) pre-plasticising the polyvinyl alcohol at a maximum temperature no higher than its softening point so as to produce a pre-plasticised polyvinyl alcohol having a melting point below the softening point of the polyvinyl alcohol used, and ii) further processing the pre-plasticised polyvinyl alcohol thus produced at a temperature above its melting point, under shear-stress conditions and for a period of time such as to produce a substantially homogeneous melt.		

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METHOD OF PRODUCING PLASTICISED POLYVINYL ALCOHOL, AND ITS USE.

The present invention relates to a method of producing plasticised polyvinyl alcohol and to its use in processes for the preparation of thermoplastic polymeric compositions which include starch and polyvinyl alcohol and are suitable for the production of films and moulded or extruded articles having good biodegradability characteristics.

The production of films based on starch and polyvinyl alcohol by casting and simple extrusion processes is known.

In this connection, US patent 3,316,190 is directed towards the production of non-cling, water-soluble films by the casting of an aqueous solution containing polyvinyl alcohol, starch and a surfactant.

US patent 3,472,804 describes the production of films which are insoluble in water by the casting of compositions including polyvinyl alcohol of high or medium molecular weight, starch or, preferably, dextrin, polymerisable derivatives of formaldehyde, more precisely, urea-formaldehyde or phenol-melamine reaction products, and a plasticiser.

US patent 3,949,145 describes the production of biodegradable films useful as mulching by the casting of aqueous solutions of polyvinyl alcohol, starch and glycerine. The water-resistance of these films is improved by a water-resistant polymeric coating.

US patent 3,312,641 describes the use of polyvinyl alcohol as a plasticiser for amylose or starches with amylose contents of more than 50%. The compositions are converted into films by casting or by simple extrusion with the use of an extruder with a filming orifice.

It will be appreciated that the production techniques described above are expensive and not very suitable for large-scale industrial production.

Film-forming, biodegradable polymeric compositions including starch and thermoplastic polymers which are insoluble, or relatively insoluble, in water, possibly in combination with hydrophilic polymers which are soluble in water, have recently been described. These compositions enable films and moulded articles with improved mechanical characteristics to be produced by processes which are conventional in relation to thermoplastic materials. In this connection, EP-A-0 400 532 describes compositions including starch and an ethylene-vinyl alcohol copolymer which may include up to 15% by weight of polyvinyl alcohol with reference to the total weight of the composition, and a plasticiser. These compositions are prepared by blending the components in the presence of a limited water content and/or of a plasticiser preferably in an extruder heated to a temperature such as to form a thermoplastic melt. In the compositions of the patent application cited above, the use of polyvinyl alcohol in combination with starch and with the polymer which is insoluble or relatively insoluble in water, enables the water-resistance of the articles to be modulated according to the use for which the articles are intended. Thus, for example, the use of polyvinyl

alcohol is desirable for the production of articles disposable in water ("flushable" articles), such as sanitary articles, in particular.

The difficulties connected with the thermoplastic processing of polyvinyl alcohol, which has a high melting point and is subject to thermal decomposition below its softening point, however, are known. The need to reduce the softening point of polyvinyl alcohol intended for thermoplastic processing is thus known.

US patent 4,542,178 describes a method of producing polyvinyl alcohol granules which contain a plasticiser and are suitable for thermoplastic processing, the method requiring the use of granular polyvinyl alcohol of a particular particle size. The plasticising method provides for the granular polyvinyl alcohol to be mixed, in the presence of a quantity of water which is insufficient to dissolve the polyvinyl alcohol, and of a plasticiser, in a mixer with forced circulation (a turbomixer). The method is carried out by subjecting the polyvinyl alcohol to a heating cycle in which its temperature is raised to a value no higher than 140°C and is then reduced to a value of about 40-70°C so as to cause the bulking of the particles, their temporary agglomeration, and the subsequent disintegration of the agglomerations. In a preferred embodiment, the granular polyvinyl alcohol is mixed in the presence of a compound which has a high molecular weight and is soluble or dispersible in water, such as starch or cellulose derivatives. The plasticised granular polyvinyl alcohol thus produced can be subjected to thermoplastic processing by conventional injection-moulding or extrusion processes for producing shaped articles and films.

The tests carried out by the Applicant have shown, however, that the granular polyvinyl alcohol produced according to the technology of US patent 4,542,178 is not suitable for use in starch formulations including a synthetic thermoplastic polymer which is insoluble or relatively insoluble in water, such as those described in patent application EP-A-400,532, since films produced by the extrusion and blowing of such formulations have many large non-fused lumps of polyvinyl alcohol which adversely affect their physical-mechanical characteristics.

An object of the present invention is therefore to provide a new method of plasticising polyvinyl alcohol so as to provide a pre-plasticised polyvinyl alcohol which is suitable for thermoplastic processing and, in particular, is suitable for incorporation in starchy formulations including thermoplastic polymers which are insoluble or relatively insoluble in water.

For this purpose, a subject of the invention is a method of producing plasticised polyvinyl alcohol by mixing polyvinyl alcohol, in the presence of an organic plasticiser and water in a quantity which is insufficient to dissolve the polyvinyl alcohol under normal conditions, characterised in that it includes the steps of:

- pre-plasticising the polyvinyl alcohol at a maximum temperature no higher than its softening point so as to produce a pre-plasticised polyvinyl alcohol having a melting point below the softening point of the polyvinyl alcohol used, and
- further processing the pre-plasticised polyvinyl

alcohol thus produced at a temperature above its melting point under shear-stress conditions and for a period of time such as to produce a substantially homogeneous melt.

The polyvinyl alcohol used in the method of the invention is prepared, in known manner, by saponification, preferably by the hydrolysis of polyvinyl esters, preferably polyvinyl acetate, and has the following characteristics:

molecular weight: 50,000-120,000

degree of hydrolysis: 60-99%, preferably 75-98%.

The method of the invention is preferably carried out with the use of an extruder, the chamber of which has at least two regions in which the temperature is controlled. The first plasticising step of the method can thus be carried out in one or more regions of an extruder in which the temperature is controlled so that the material supplied is kept at a temperature no higher than 200°C, preferably from 60 to 180°C, and in which the screw has a transportation and plasticising profile. The second step of the method is carried out in one or more regions of the extruder in which the temperature is kept above the melting point of the pre-plasticised polyvinyl alcohol produced in the first region of the extruder. Typically, in the second step of the method, the temperature is above 140°C and generally between 140 and 210°C.

In this embodiment of the method, it is preferable to use an extruder with two screws which ensures higher shear-stress values than a single-screw extruder.

In the second mixing step which is carried out at a temperature above the melting point, the time spent in the extruder is typically within a range of from 30 to 500 seconds, with the application of a shear stress such as to produce a substantially homogeneous melt. The temperature of the melt is then preferably reduced and, at the nozzle, the melt is kept at a temperature generally no higher than 170°C.

The melt can be extruded in rod form and cooled in air or may be supplied directly to an extruder for blow-extrusion.

In the course of the process which takes place in the extruder, the water content may be reduced by degassing, upstream of the extrusion orifice, preferably during the second plasticising step, to obtain a water content in the melt generally of between 5 and 20% by weight.

If the method is carried out in a single- or double-screw extruder, the polyvinyl alcohol supplied may be in the form of granules, flakes, or powder.

Alternatively, the pre-plasticising step i) may be carried out under mixing conditions typical of a slow mixer with the use of flaked or powdered polyvinyl alcohol (PVA) or under the mixing conditions of a fast mixer (a turbomixer), particularly if flaked PVA is used; in these cases the maximum temperature in the slow mixer or in the turbomixer does not exceed 140°C.

The pre-plasticised product is then subjected to the second mixing step described above in a double-screw or single-screw extruder.



7

The concentration of the organic plasticiser is generally within the range of from 5 to 50 parts by weight, preferably 15-40%, with reference to the weight of the polyvinyl alcohol. The preferred plasticisers include aliphatic polyols and their acetate, ethoxylate and propoxylate derivatives, particularly glycerine, ethylene or propylene glycol, ethylene or propylene diglycol, ethylene or propylene triglycol, polyethylene glycol, polypropylene glycol, 1,2-propandiol, 1,3-propandiol, 1,2-, 1,3-, 1,4-butandiol, 1,5-pentandiol, 1,6-, 1,5-hexandiol, 1,2,6-, 1,3,5-hexantriol, neopentyl glycol, trimethylol propane, pentaerythritol, sorbitol and the acetate, ethoxylate and propoxylate derivatives thereof, particularly sorbitol ethoxylate, pentaerythritol ethoxylate, sorbitol acetate, and pentaerythritol acetate. A mixture of several plasticisers may be used.

The water concentration is generally between 2 and 40% by weight, preferably from 15 to 40% by weight, with reference to the polyvinyl alcohol.

The polyvinyl alcohol produced by the method of the invention has a melting point of between 110 and 160°C, preferably between 120 and 140°C, and is particularly suitable for the preparation of film-forming compositions including starch and polyvinyl alcohol, or starch, polyvinyl alcohol and one or more synthetic thermoplastic polymers which are insoluble or relatively insoluble in water.

The methods of producing the aforementioned compositions with the use of plasticised polyvinyl alcohol according to the method described above

constitute further subjects of the invention.

Polymeric compositions including starch and a synthetic thermoplastic polymer which can be transformed into shaped articles or films are described in patent applications W090/10671, W091/02025, W091/2024 and EP-A-0 400 532.

In the present description, thermoplastic polymers which are insoluble or relatively insoluble in water means polymers and copolymers which absorb no more than 15% by weight of water at 20°C and at equilibrium. Preferred polymers are polymers and copolymers which are derived from ethylenically unsaturated monomers and which have repeating units with at least one polar functional group such as a hydroxy, alkoxy, carboxy, carboxyalkyl, alkylcarboxy or acetal group. Preferred polymers include copolymers of an olefin selected from ethylene, propylene, isobutene and styrene with acrylic acid, vinyl alcohol and/or vinyl acetate. These olefin copolymers include, in particular, ethylene copolymers such as ethylene-acrylic acid, ethylene-vinyl alcohol, ethylene-vinyl acetate and mixtures thereof. Particularly preferred are ethylene-vinyl alcohol copolymers with ethylene contents of from 10 to 44% by weight, produced by the hydrolysis of the corresponding ethylene - vinyl acetate generally with a degree of hydrolysis of between 50 and 100%.

The synthetic polymeric component may also include epsilon-polycaprolactone and copolymers thereof, polyhydroxybutyrate/valerate and polymers and copolymers of lactic acid with glycolic acid or caprolactone.

The starch used in these polymeric compositions is preferably a native starch, particularly maize or potato starch. The term "native" includes starches with high amylose contents and "waxy" starches. It is, however, possible to use physically and chemically modified starches such as starch ethoxylates, starch acetates, cationic starches, oxidised starches and cross-linked starches. The native starch is normally used in the preparation of the formulations without being dried beforehand and has an intrinsic water content of about 9-15% by weight.

The method of preparation with the use of plasticised polyvinyl alcohol does not differ substantially from known methods already described in the patent literature cited above. In fact, the compositions are prepared by mixing the components in an extruder which is heated to a temperature sufficient to produce a thermoplastic melt. In addition to the plasticiser present in the polyvinyl alcohol, the composition supplied to the extruder may include a further quantity of plasticiser useful for plasticising the starch and any synthetic thermoplastic polymer used. Generally, the total quantity of plasticiser is between 1 and 50% by weight, preferably between 5% and 25% by weight, with reference to the weight of the total composition.

The plasticisers used may be the same plasticisers which are used in the preliminary plasticising of the polyvinyl alcohol, or a mixture thereof.

A total quantity of up to 40% by weight of water, with reference to the starch-water system, may be added to the composition supplied to the extruder; however, in the presence of a high-boiling plasticiser, the

intrinsic water content present in the starch used is sufficient per se to cause the formation, under the process conditions, of a thermoplastic melt in which starch, synthetic polymer and polyvinyl alcohol are interpenetrated at the molecular level.

The material supplied to the extruder may also include agents, such as urea, which can destroy the hydrogen bonds, and of which a quantity of 0.5 to 20 % by weight, preferably between 2 and 7% by weight with reference to the total composition, can be added to the mixture of starch and polymers.

The polymeric material may also include cross-linking agents, such as aldehydes, ketones and glyoxals, process coadjuvants, release agents, and lubricants, such as fatty acids, esters of fatty acids, higher alcohols and polyethylene waxes which are normally incorporated in moulding and extrusion compositions, antioxidants, opacifiers and stabilisers.

Small quantities, generally no greater than 5% by weight, with reference to the weight of the total composition, of hydrophobic polymers such as polyethylene, polypropylene, polystyrene may also be included in the formulations.

The pressures to which the mixture of the components cited above is subjected during the heat treatment are those typical for extrusion in a single or double-screw extruder. However, although the process is preferably carried out in an extruder, the mixing may be effected in any device which ensures temperature and shear-stress conditions sufficient to render the starch and the polymeric fraction compatible from a

rheological point of view. The preferred method of preparing the compositions with the use of the plasticised polyvinyl alcohol includes the steps of:

- bulking the starch and the synthetic polymer by means of the plasticiser available and possibly the water present, at a temperature of between 80 and 180°C; this effect may be achieved, for example, during a first stage of the transportation of the components through an extruder, for a period of time of the order of from 2 to 50 seconds,
- subjecting the mixture to shear-stress conditions corresponding to similar viscosity values of the polymeric and starchy components so as to favour the interpenetration of the molecules of the components,
- degassing the mixture freely, under controlled pressure conditions or under vacuum, to produce a melt at a temperature of from 135 to 180°C with a water content such that bubbles are not created at atmospheric pressure, that is, for example, at the output of the extruder.

The melt may then be extruded directly in the form of a film with the use of an extruder with a blowing head, or may be extruded and transformed into pellets for subsequent processing by conventional extrusion, extrusion and blowing, or injection moulding techniques.

The preferred compositions include polyvinyl alcohol plasticised according to the invention including the following percentages by weight of the components:

12

- starch (anhydrous): 20-70%, preferably 30-60%,
- total synthetic polymer: 5-50%, preferably 20-40%.
- total plasticisers: 5-25%,
- urea: 0-7%, preferably 2-5%,
- water (extruded, not conditioned): 2-6%.

The polyvinyl alcohol generally constitutes from 10 to 100% and preferably from 20 to 50% by weight of the total synthetic polymeric component. As an absolute value, the concentration of the polyvinyl alcohol in the compositions is preferably between 2 and 25% by weight.

#### Examples 1-3

A) Plasticising in a double-screw extruder.

The polyvinyl alcohol (referred to as PVA below) was plasticised with the use of an extruder Model EPV 60/36D with two corotating screws and 9 heating zones in which the following heating profile was established:

60-100-180-200-200-200-190-170-150°C

The polyvinyl alcohols used were the product POLYVIOL G40/140 (registered trade mark, Wacker) and the product GOHSENOL GH23 (registered trade mark, Nippon Gohsei) in flake and powder form, respectively. The extruder was supplied with an aqueous solution of glycerine preheated to a temperature of 60°C and including a percentage by weight of glycerine, with reference to the polyvinyl alcohol, of between about 27% and about 40%, and water, with a glycerine/water ratio of 4.3 and 1 by weight in the various examples. The extrusion

13

was carried out at a rate of rotation of 125 RPM and with a flow rate of 50 kg/h which corresponds to a period of about 48 seconds spent in the extruder. The material in the extruder was subjected to a first mixing and transportation step in the region corresponding to the zone in which the temperature was set at 60 and 100°C with an estimated time of about 20 seconds spent in those zones, so as to pre-plasticise the polyvinyl alcohol; in the subsequent zones, the temperature was gradually brought to a maximum of 200°C (set temperature) and the temperature was then reduced before extrusion which was carried out at a temperature of about 160°C; the material extruded in rod form was cooled in air.

The operative characteristics and the characteristics of the plasticised PVA, determined by DSC, are given in Table 1.

#### Examples 4-12

##### C) Formulation of thermoplastic compositions.

The plasticised polyvinyl alcohol produced by the method of each of Examples 1 to 3 was used to prepare thermoplastic compositions with ethylene-vinyl alcohol in the formulations A, B and C of Table 2, in which the individual components are indicated in parts by weight, thus producing nine thermoplastic compositions which were used to produce films by extrusion and blowing.

The thermoplastic compositions were prepared with the use of an EPV 60/36D extruder with two corotating two-stage screws operating at 150 RPM, and in which the following heating profile was established:

14

90 -140-175-175-175-175-165-135°C with a flow-rate of 80 kg/h. The water content of the composition supplied to the extruder, which was derived from the intrinsic water content of the starch used and from the solution of plasticisers, was reduced by degassing during the extrusion to obtain a water content of about 5% by weight in the extruded material.

D) Preparation of films by extrusion-blowing.

The extruded material in rod form was reduced to pellets which were used in extrusion and blowing with the use of an extruder having the following characteristics:

model: Ghioldi, having a single screw with a diameter of 40 mm and L/D of 30,  
screw profile: constant taper, compression ratio 1:2.8,  
blowing head: diameter 100 mm, decompressed  
distributor: spiral  
heating profile set: 135-135-140-140-140-140-145-145°C.

The films produced by extrusion and blowing were examined optically to evaluate the presence of fused lumps and the evaluations for each film are given in Table 3.

Examples 13-16

The plasticising method was carried out with the first mixing step being effected in a slow mixer and the second mixing step in a single-screw extruder.



A1) Mixing in a slow mixer

A BATTAGGION ME100 direct-current slow mixer was used, operating under the conditions given in Table 4.

The plasticisers used were aqueous solutions of glycerine of the percentage concentrations by weight indicated in Table 4. The plasticisers were injected by means of two atomising injections; the second injection was effected after the first portion had been fully absorbed. It was noted that the injection of hot plasticiser gave rise to a high degree of bulking of the PVA load such as to limit the loading capacity of the mixer. The use of powdered PVA is preferable for this technique; granular PVA such as, for example, POLYVIOL G40/140 (registered trade mark, Wacker) makes it difficult for the plasticiser to penetrate and produces a wet and sticky paste, because it has less surface area in contact with the liquid. The mixing was carried out at a temperature of from 20 to 60°C for a period of 120 minutes to produce a friable powder or a powder with small agglomerations.

The final product was then plasticised further with the use of a single-screw extruder.

B1) Single-screw plasticising

A single-screw extruder having the following characteristics was used:

model: OMC with a screw diameter of 60 mm and an L/D of 35

screw: double metering type with degassing

screw speed: 35-50 RPM

16

heating profile set: 120-185-205-205-200-190-180°C.

The characteristics of the plasticised PVA produced were determined by DSC and are given in Table 5.

C1)-D1) Preparation of thermoplastic compositions and extrusion-blowing

The plasticised PVA was used to prepare thermoplastic compositions according to formulation C in Table 2, working under the conditions given in paragraph C) for Examples 4-12 and the compositions produced were used to produce films by extrusion and blowing by the method given in paragraph D) of Examples 4-12. The films produced were examined for the presence of non-fused lumps which were found to be absent or extremely rare and such as not to cause substantial non-homogeneity of the films produced. The evaluations are given in Table 5.

Examples 17-25

In these tests the polyvinyl alcohol was plasticised with the first mixing step being carried out in a turbomixer and the pre-plasticised product being supplied to a single-screw extruder in order to carry out the second step.

A2) Plasticising in a turbomixer

A 10 l direct-current Plasmec model turbomixer was used with the use of flaked POLYVIOL G40/140 (registered trade mark, Wacker) polyvinyl alcohol. The plasticiser used was glycerine mixed with water and the

17

plasticiser was introduced by sprinkling or was atomised.

The operative conditions and the characteristics of the product obtained, determined by DSC, are given in Table 6.

#### B2) Single-screw plasticising

The product obtained as a result of plasticising in the turbomixer was supplied to a single-screw extruder having a 20 mm diameter single "metering" type screw with an L/D of 35 and a compression ratio of 1 to 3. The extrusion was carried out at a rate of rotation of 60 RPM with the following heating profile set: 150-200-205-205-180°C.

#### C2) Preparation of thermoplastic compositions

The plasticised PVA was used to prepare thermoplastic compositions according to the formulation C given in Examples 4-12 with the use of a single-screw extruder having a "metering" type screw with a compression ratio of 1:3, a diameter of 20 mm and an L/D of 35, operating at 60 RPM with the following heating profile set: 90-160-180-140-130°C. The plasticised polyvinyl alcohol was used in a formulation corresponding to the formulation C given in Examples 4-12.

#### D2) Extrusion-blowing

The thermoplastic compositions obtained in the form of pellets were used in extrusion and blowing with the use of a HAAKE extruder with a single screw having a diameter of 19.05 mm and an L/D of 25, operating at a

18

rate of rotation of 64 RPM with a 20 mm-diameter blowing head and a blowing ratio of 4.4. Heating profile set: 140-145-145-155°C.

The films obtained were examined optically to evaluate the presence of fused lumps; those present, however, had very small dimensions of between 0.1 and 0.5 mm and were such as to have only a slight adverse affect on the mechanical characteristics of the films produced. The characteristics relating to the films obtained according to examples 17-25 are given in Table 7, together with the results of the analysis of the fused lumps present, determined by DSC.

Examples 26-34 (comparative)

The plasticised PVA obtained as a result of plasticising in a turbomixer according to Examples 17-25 was used directly to produce thermoplastic compositions which were then transformed into films by the methods C2) and D2) described in connection with Examples 17-25. The films produced were evaluated for the presence of non-fused lumps and very many non-fused lumps with dimensions of up to 3 mm were found; the number of non-fused lumps of polyvinyl alcohol present in all the tests was such as to have an adverse effect on the characteristics of the films which were in any case of very poor quality and unacceptable.

19  
TABLE 1

## PLASTICISATION OF PVA IN A DOUBLE-SCREW EXTRUDER

Example	1	2	3
PVA: type	POLYVIOL G40/140	POLYVIOL G40/140	POLYVIOL GH23
concentration PVA (%)	67	65	65
GLYCERINE %	26.8	17.5	17.5
WATER	6.2	17.5	17.5
CHARACTERISTICS OF PLASTICISED PVA GRANULES			
$T_m$ °C	148	120	120
$\Delta H_m$ J/g	16	12	8
$T_c$ °C	76	43	50
$\Delta H_c$ J/g	-12	-5	-7
residual $H_2O\%$	n.d.	8-12	n.d.

n.d.: not determined

 $T_m$ : melting point $T_c$ : crystallisation point

20  
TABLE 2

## THERMOPLASTIC COMPOSITIONS (EXAMPLES 4-12)

	A	B	C
GLOBE STARCH (CERESTAR) (H <sub>2</sub> O CONTENT 10% by weight)	38	36	36
EVOH (1)	26	26	26
UREA	4.5	4.5	5
PLASTICISED PVA (examples 1 - 3)	10.4	10.4	10.4
PLASTICISERS	13 (2)	15 (3)	17 (4)

(1) ethylene-vinyl alcohol 44% by weight ethylene

(2) 81.2% by weight glycerine, 18.8% by weight H<sub>2</sub>O

(3) 100% glycerine

(4) sorbitol ethoxylate 11.2% by weight  
H<sub>2</sub>O 3.74% by weight  
glycerine 2.04% by weight

21  
TABLE 3

QUALITY OF THE FILM BY PRESENCE OF NON-FUSED LUMPS

(EXAMPLES 4-12)

Ex. formul.	1	2	3
A	good	very good	very good
B	good	very good	very good
C	good	very good	very good

Legend: Evaluations of the films on the basis of the number of non-fused lumps per m<sup>2</sup> of film and their dimensions.

- Film very good: - fewer than 100 non-fused lumps all smaller than 0.1mm
- Film good: - between 1 and 10 non-fused lumps of between 0.5 and 0.1mm  
- between 100 and 150 non-fused lumps smaller than 0.1mm
- Film fair: - fewer than 5 non-fused lumps of between 0.5 and 1.5mm  
- more than 10 non-fused lumps of between 0.5 and 0.1mm
- Film unacceptable: - presence of non-fused lumps of between 1 and 1.5mm
- Film very poor: - non-fused lumps larger than 1.5mm.

22  
TABLE 4PLASTICISATION IN A SLOW MIXER AND  
A SINGLE-SCREW EXTRUDER (EXAMPLES 13-16)

EXAMPLE	13	14	15	16
PVA: type	GOHSENO GH 17			
% by weight	70	70	60	64
glycerine % by weight	15	15	20	18
water % by weight	15	15	20	18
plasticising T °C	20	60	20	60
chamber T °C	20	60	20	60
Final product: appearance	F.P.	small/medium AGGL	F.P.	small/medium AGGL
apparent density g/cm <sup>3</sup>	0.52	0.4	0.38	0.30

F.P. = friable powder

AGGL = agglomerations



TABLE 5

CHARACTERISTICS OF PVA PLASTICISED IN A SLOW MIXER AND A  
SINGLE-SCREW EXTRUDER AND EVALUATION OF THE FILMS

Example	13	14	15	16
$T_m$ ( $^{\circ}\text{C}$ )	147	154	133	145
$\Delta H_m$ (J/g)	18	19	60	80
$T_c$ ( $^{\circ}\text{C}$ )	85	89	60	80
$\Delta H_c$ (J/g)	-15	-17	-7	-14
Residual $\text{H}_2\text{O}$	4.1	3.4	7.3	5.2
Colour	Trasp./ grey	Trasp./ yellow	Trasp./ grey	Trasp./ yellow
evaluation of the film	good	good	very good	very good

TABLE 6  
PLASTICISATION IN A TURBOMIXER (EXAMPLES 17-25)

Example	glycerine (% by weight)	water (% by weight)	speed of blades (rpm)	final physical condition	DSC Analysis			
					T <sub>m</sub> (°C)	H <sub>m</sub> (J/g)	T <sub>c</sub> (°C)	H <sub>c</sub> (J/g)
17	11.25	3.75	1600	F.P.	-	-	-	-
18	15	5	"	F.P.	155	45	72	-12
19	18.75	6.25	"	AGGL	159	32	75	-13
20	22.5	7.5	"	AGGL	131	30	57	-8
21	26.25	8.75	"	AGGL	120	18	44	-6
22	17.5	2.5	"	F.P.	-	-	-	-
23	15	5	"	F.P.	-	-	-	-
24	12.5	7.5	"	F.P.	-	-	-	-
25	10	10	"	S.AGGL	-	-	-	-

AGGL = agglomerated

S.AGGL = slightly agglomerated

F.P. = friable powder

TABLE 7

EVALUATION OF THE FILMS OF PVA PLASTICISED IN A TURBOMIXER WITH A SINGLE-SCREW EXTRUDER

Examples	Evaluation of the film	Analysis of fused lumps			
		$T_m$ (°C)	$\Delta H_m$ J/g	$T_c$ °C	$\Delta H_c$ J/g
17	fair	129	12	86	-12
18	fair	-	-	-	-
19	fair	-	-	-	-
20	good	128	9.7	86	-6
21	very good	127	15	84	-10
22	fair	131	13	87	-7
23	fair	127	13	85	-12
24	fair	130	6.6	113	-13
25	fair	129	12	88	-8

26  
CLAIMS

1. A method of producing plasticised polyvinyl alcohol by mixing polyvinyl alcohol, in the presence of an organic plasticiser and water in a quantity which is insufficient to dissolve the polyvinyl alcohol under normal conditions, characterised in that it includes the steps of:

i) pre-plasticising the polyvinyl alcohol at a maximum temperature no higher than its softening point so as to produce a pre-plasticised polyvinyl alcohol having a melting point below the softening point of the polyvinyl alcohol used, and

ii) further processing the pre-plasticised polyvinyl alcohol thus produced at a temperature above its melting point under shear-stress conditions and for a period of time such as to produce a substantially homogeneous melt.

2. A method according to Claim 1, in which steps i) and ii) are carried out in a heated extruder including at least one first mixing and transportation region which is kept at a temperature below 200°C and at least one second mixing and transportation region which is kept at a temperature above the melting point of the pre-plasticised polyvinyl alcohol produced in the first region.

3. A method according to Claim 1, in which step i) is carried out in a mixer with forced circulation at a maximum temperature no higher than 140°C and step ii) is carried out in an extruder.

4. A method according to Claim 1, in which step i) is carried out in a slow mixer at a temperature no higher than 140°C and step ii) is carried out in an extruder.
5. A method according to Claim 2, in which the extruder has two corotating screws.
6. A method according to any one of Claims 1 to 5, in which the mixing is carried out in the presence of a concentration of plasticiser of from 5 to 50% by weight, preferably from 15 to 40% by weight, with reference to the polyvinyl alcohol.
7. A method according to Claim 6, in which the plasticiser is selected from the group consisting of glycerine, ethylene/propylene glycol, ethylene/propylene diglycol, ethylene/propylene triglycol, polyethylene glycol, polypropylene glycol, 1,2-propandiol, 1,3-propandiol, 1,2-, -1,3-, 1,4-butandiol, 1,5-pentandiol, 1,6-, 1,5-hexandiol, 1,2,6-, 1,3,5-hexantriol, neopentyl glycol, trimethylol propane, sorbitol, pentaerythritol, sorbitol ethoxylate, pentaerythritol ethoxylate, sorbitol acetate, pentaerythritol acetate and mixtures thereof.
8. A method according to any one of Claims 1 to 7, in which water is present at a concentration of from 2 to 40% by weight with reference to the weight of the polyvinyl alcohol supplied.
9. A method according to any one of Claims 1 to 8, in which the step (ii) is carried out at a temperature of between 140 and 210°C.
10. The use of the plasticised polyvinyl alcohol

28

produced according to any one of Claims 1 to 9 for the preparation of polymeric compositions including polyvinyl alcohol and starch.

11. A method of producing biodegradable polymeric mixtures including starch, at least one synthetic thermoplastic polymer which is substantially insoluble in water, polyvinyl alcohol and a plasticiser by mixing the components in the presence of a water content of between 5 and 40% by weight, with reference to the sum of the starch and the water, under temperature and pressure conditions such as to form a thermoplastic melt, characterised in that the polyvinyl alcohol used is pre-plasticised polyvinyl alcohol produced according to any one of Claims 1 to 9.

12. A method according to Claim 11, in which the synthetic thermoplastic polymer is a polymer of at least one ethylenically unsaturated monomer, the polymer including repeating units having at least one polar group selected from the group consisting of hydroxy, alkoxy, carboxy, carboxyalkyl, alkylcarboxy and acetal groups.

13. A method according to Claim 12, in which the synthetic thermoplastic polymer is a copolymer of an olefin selected from the group consisting of ethylene, propylene, isobutene and styrene with acrylic acid, vinyl alcohol or vinyl acetate.

14. A method according to Claim 13, in which the synthetic thermoplastic polymer is an olefinic copolymer selected from the group consisting of ethylene-vinyl alcohol having an ethylene content of from 10 to 44% by weight and a degree of hydrolysis of

from 50 to 100%, ethylene-acrylic acid and mixtures thereof.

15. A method according to Claim 11, in which the synthetic polymer includes epsilon-caprolactone or copolymers thereof, polyhydroxybutyrate, polyhydroxybutyrate/valerate or polymers of lactic or glycolic acid.

16. A method according to any one of Claims 11 to 16, in which the biodegradable polymeric mixture includes:

from 20 to 70% by weight of starch (anhydrous)  
from 10 to 50% by weight of total synthetic thermoplastic polymer, and  
from 5 to 25% by weight of an organic plasticiser.

17. A method according to Claim 16, in which the synthetic polymer includes from 10 to 50% by weight of polyvinyl alcohol.

## INTERNATIONAL SEARCH REPORT

PCT/EP 92/02517

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08K5/00; C08J3/18; C08L29/04; C08L3/02		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08K ; C08J ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	FR,A,825 552 (H. VOHRER) 13 August 1937 see claims 1-2	1
A	FR,A,2 275 517 (TORAY IND. INC) 16 January 1976 see claim 14; examples	1,3,4
<p><sup>10</sup> Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
18 FEBRUARY 1993		15. 03. 93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		Dieter Schöler



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9202517  
SA 66713

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The members are as contained in the European Patent Office EDP file on  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-825552		GB-A- 493561 US-A- 2127896	
FR-A-2275517	16-01-76	US-A- 4007152 GB-A- 1463650	08-02-77 02-02-77

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